

Electronic Supplementary Information

**Enhanced lithium storage capacity and cyclic performance of
nanostructured TiO₂-MoO₃ hybrid electrode**

Seung-Min Paek,^{a,b} Joo-Hee Kang,^a Hyun Jung,^{a,c} Seong-Ju Hwang,^a and Jin-Ho Choy^{a,*}

^a *Center for Intelligent Nano-Bio Materials (CINBM), Department of Bioinspired Sciences, and
Department of Chemistry and Nano Sciences, Ewha Womans University, Seoul 120-750, Korea*

^b *Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang 790-784, Korea*

^c *Department of Chemistry, Dongguk University, Seoul 100-715, Korea.*

* To whom all correspondence should be addressed.

Tel: +82-2-3277-4135,

Fax: +82-2-3277-4340,

e-mail: jhchoy@ewha.ac.kr.

Experimental details for X-ray absorption spectroscopy

The *in situ* X-ray absorption spectroscopy (XAS) experiments at the Mo K-edge were performed with the X-ray absorption fine structure (XAFS) facility installed at beamlines 7C in the Pohang Accelerator Laboratory, Korea. All the samples were ground to fine powder, and then, a pouch-type cell for charge/discharge was constructed, in which the nanohybrid electrodes were made by intimately mixing 70% (by weight) active nanohybrid material, 25% Ketjenblack, and 5% poly(tetrafluoroethylene). After assembled with Li foil, a separator, and a ~ 40 μm thick $\text{TiO}_2\text{-MoO}_3$ electrode, the cell was vacuum sealed with an aluminium pouch. The X-ray photon flux was enough to transmit through the electrochemical cell without any chemical interaction.

The *in situ* XAS data were collected at room temperature in a transmission mode. All the present spectra were calibrated by measuring the spectra of Mo metal foil simultaneously with those of the samples. A Si(111) double crystal monochromator was employed to monochromatize the X-ray photon energy. A step size was 0.2 eV in the XANES region in order to accurately collect the XANES spectra. Data analysis were carried out by the standard procedure as reported previously.^{1,2}

References

1. S. M. Paek, H. Jung, Y. J. Lee, M. Park, S. J. Hwang and J. H. Choy, *Chem. Mater.*, 2006, **18**, 1134.
2. S. M. Paek, H. Jung, M. Park, J. K. Lee and J. H. Choy, *Chem. Mater.*, 2005, **17**, 3492.

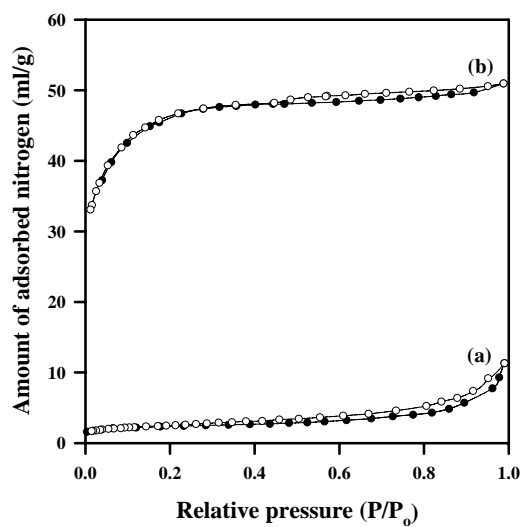


Figure S1. N₂ adsorption-desorption isotherms for (a) the restacked MoO₃ and (b) TiO₂-pillared MoO₃.

After the intercalation of TiO₂ into the interlayer spaces of MoO₃, the specific surface area was remarkably enhanced from 10 to 210 m²/g. Furthermore, the nanohybrid shows the adsorption of much large amount of nitrogen, suggesting that the pillaring reaction is very effective in enhancing the porosity of TiO₂-MoO₃.

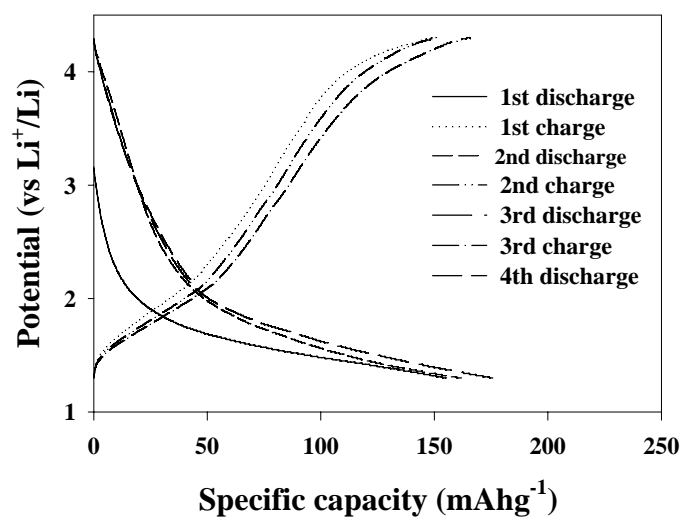


Figure S2. Charge-discharge curves of TiO₂ nanoparticle.

TiO₂ nanoparticle shows a reversible capacity of ~180 mAh/g, suggesting that TiO₂ nanoparticles could be used as spacers and/or pillars in electrode materials.

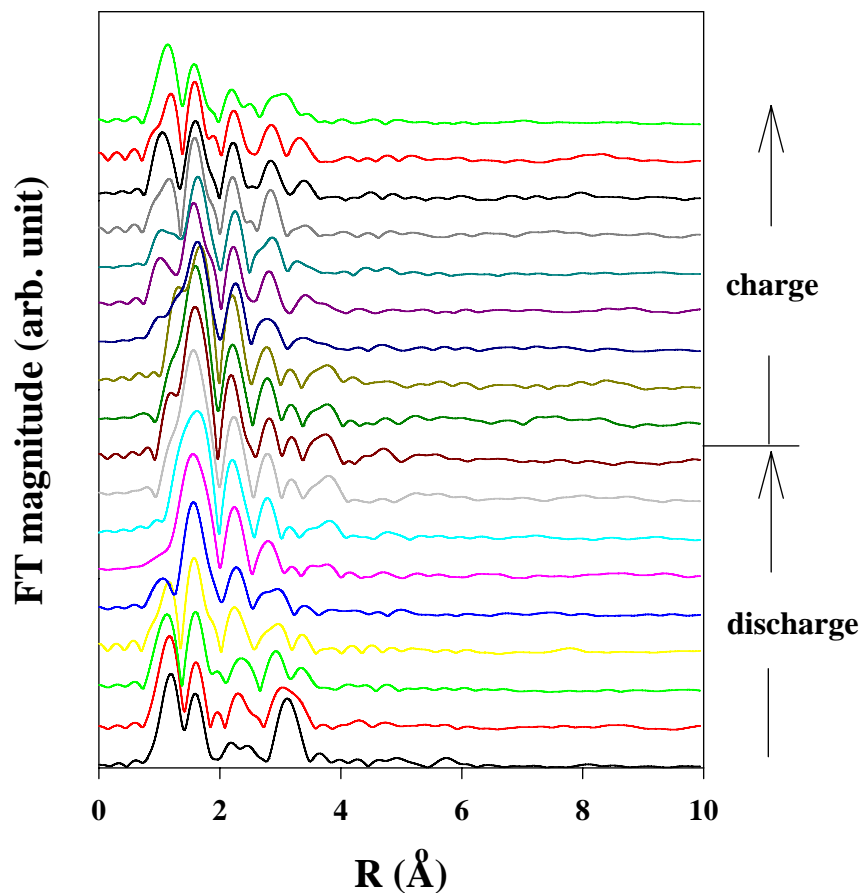


Figure S3. Fourier transforms of *in situ* Mo K-edge extended X-ray absorption fine structure (EXAFS) spectra for TiO₂-pillared MoO₃ during discharge/charge reaction.

Two FT peaks below 2 Å (non-phase-shift-corrected) can be indexed to Mo–O bonds ranged from 1.67 to 2.34 Å. The FT peaks from 3 to 4 Å are due to the Mo–Mo neighboring atoms. Before discharge (before lithium intercalation), the local structure of MoO₃ in hybrid material can be indexed as α -MoO₃, revealing the lattice frameworks of α -MoO₃ in TiO₂-pillared MoO₃ are maintained upon reassembling reaction. As the amount of the intercalated lithium ions increases, two FT peaks below 2 Å are merged into one FT peak, showing the reduction of MoO₃. However, after the full charge (lithium extraction), α -MoO₃ framework in TiO₂-pillared MoO₃ restores well, highlighting the reversible lithium intercalation reaction.

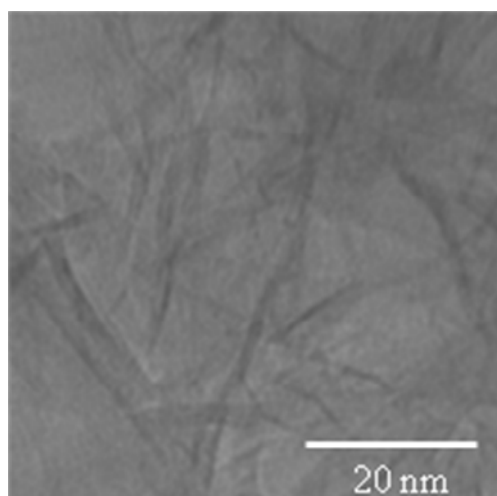


Figure S4. Cross-sectional TEM image for the exfoliated MoO₃ nanosheets.

As seen in the Figure S4, very thin layers can be attributed to the exfoliated MoO₃, clearly showing the nanosheet structure.

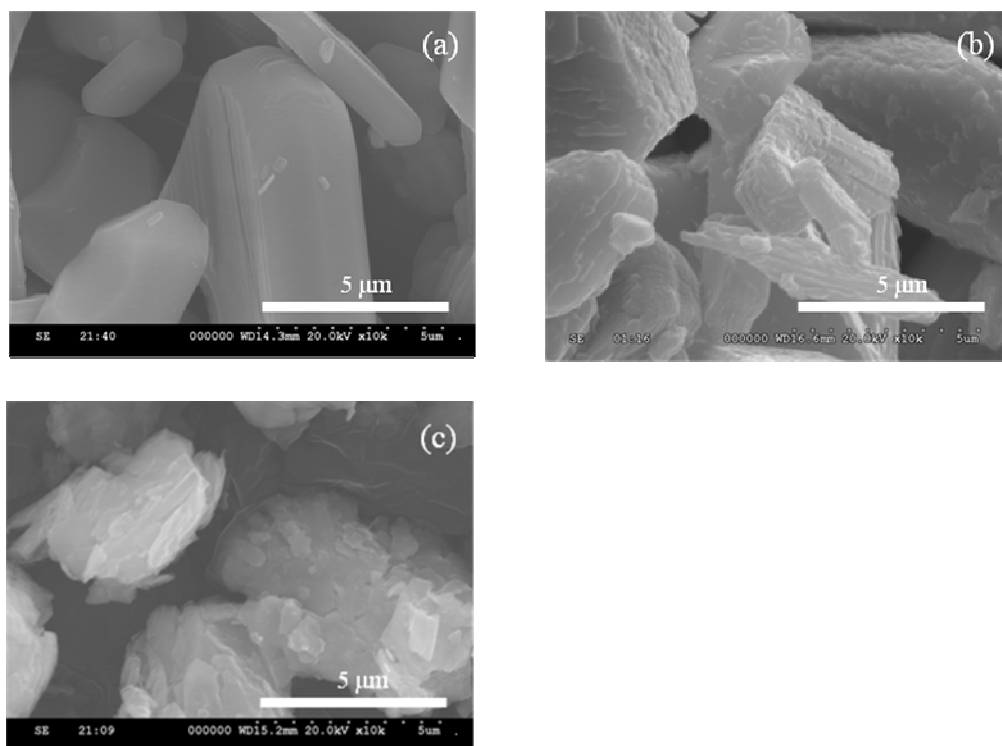


Figure S5. FE-SEM image for (a) the pristine MoO₃, (b) Li_{0.4}MoO₃ and (c) the exfoliated and restacked MoO₃.

As seen in the figure, the pristine MoO₃ has very clean and smooth surface, and the size of the pristine MoO₃ is in the range of few micrometers. After the intercalation of lithium ions, the size of crystallite is somewhat smaller, but still in the micrometer range. The edge of the Li_{0.4}MoO₃ is relatively rough due to the intercalation of lithium ions. After the exfoliation and the restacking, the overall size of crystallite becomes smaller due to the elastic deformation. The layered morphology is still maintained even after exfoliation and restacking reaction.